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## SLOW-RELEASE FRAGRANCE AGENTS

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[There are no amendments to this patent.]

Claims

1. Slow-release fragrance agents, made by impregnating blended fragrances comprising multiple fragrance components into composite impregnable bodies comprising one, two or more kinds of thermoplastic resins for fragrance impregnation and carriers for fragrance impregnation,

or into sintered bodies made of ethylene-vinyl acetate copolymers, and impregnating the fragrance components of relatively low polarity in the blended fragrance primarily in the thermoplastic resins for fragrance impregnation or in the resin portions of the above sintered bodies, and impregnating the fragrance components of relatively high polarity in the above blended fragrance primarily in the carriers for fragrance impregnation or placing [them] primarily in the spaces in the above sintered bodies.

2. Slow-release fragrance agents described as in Claim 1, characterized by the fact that the above thermoplastic resins for fragrance impregnation are selected from a group comprising polyethylene, ethylene-vinyl acetate copolymers, ethylene-ethyl acrylate copolymers, polyvinyl chloride, polyvinyl acetate, polyethyl and methyl acrylate, polyethyl and methyl methacrylate, polyamide, polypropylene and polystyrene.

3. Slow-release fragrance agents described in Claim 1, characterized by the fact that the above carriers for fragrance impregnation are selected from a group comprising inorganic porous materials such as gypsum, silicate salts, active carbon, ceramic, alumina, etc., and filter paper, nonwoven fabric, felt and boards.

#### Detailed explanation of the invention

This invention concerns slow-release fragrance agents comprising thermoplastic resins for fragrance impregnation and carriers for fragrance impregnation, or sintered bodies of ethylene-vinyl acetate copolymer. More specifically, it concerns slow-release fragrance agents manufactured by impregnating blended fragrances comprising multiple fragrance components into composite impregnable bodies comprising one, two or more kinds of thermoplastic resins for fragrance impregnation and carriers for fragrance impregnation, or into sintered bodies of ethylene-vinyl acetate copolymers which contain spaces, and which release the multiple fragrance components over long periods with a constant aroma.

There is a large variety of about 4000 kinds of organic compounds (called single fragrances below) which are used as starting materials for fragrances, and their saturated vapor pressures are distributed over a wide range from 100 mm Hg to  $1 \times 10^{-6}$  mm Hg. [They] are highly sought after, and to create well-balanced blended fragrances, multiple single fragrances must be selected and used so that the vapor pressures of these single fragrances are continuous. Due to disparity of vapor pressures in said blended fragrances, when, for example, blended fragrances are impregnated in scented papers and left, their aromas change over time because the single fragrances vaporize in order from the single fragrances with high vapor pressures.

In the case of fragrance agents for the purpose of perfuming and deodorizing, because it is desirable that the initial aroma and the aroma during use be uniform,

(1) methods of reducing partial pressure of fragrances using odorless solvents,

(2) methods of suppressing volatility by impregnating fragrances in impregnable bodies such as synthetic polymer resins, porous inorganic compounds, fibers or wood,  
(3) methods of promoting volatilization by using several single fragrances of high vapor pressure or suppressing their volatilization by separating them,  
(4) methods of constantly supplementing the fresh fragrance using capillary action,  
etc., are used to compensate for the above drawbacks. But these drawbacks have not been resolved with any of the methods of maintaining the initial aroma by slow release of high-vapor-pressure single fragrances.

Japanese Kokai Patent Application No. Sho 56[1981]-91754 presents a method, when obtaining blended fragrances comprising 2 or more fragrance components, for volatilizing multiple fragrance components over a long period at a constant aroma by dividing the various fragrance components which constitute the blended fragrance in 2 or more groups according to the magnitudes of their vapor pressures and allowing prescribed volatilization areas for each of said groups.

Japanese Kokai Patent Application No. Sho 57[1982]-203444 presents solid fragrance agents, wherein blended fragrances are divided into two or more components according to boiling point, high-boiling-point components are impregnated into substrates from which volatilization is relatively difficult and low-boiling-point components are impregnated into substrates from which volatilization is relatively easy [sic] and the various components are volatilized from the various substrates in a balanced manner.

However, these methods had the drawback that the complicated procedures of dividing fragrance component groups by the magnitudes of their vapor pressures (boiling points) and impregnating the divided components separately into substrates had to be performed.

The inventors focused on the facts that single fragrances of low physicochemical polarity are generally easily impregnable in thermoplastic resins, and that single fragrances of low polarity generally are easily volatilized. Using these phenomena, [they] perfected an invention of slow-release fragrance agents which could maintain a constant aroma over long periods.

The focus of the inventors was based on the strength of chemical structural affinity of single fragrances for thermoplastic resins. This concept differs fundamentally from methods focusing on the vapor pressures or boiling points of single fragrances that are presented in the above patent journals.

Generally, hydrocarbons, ethers and esters are among components of relatively low polarity. Because affinity with thermoplastic resins that are used in this invention is good, [they] are easily impregnated in the above resins and can also be impregnated in the carriers for fragrance impregnation used in this invention.

Moreover, lactones, alcohols, aldehydes and ketones are among components of relatively high polarity. Because affinity with the thermoplastic resins used in this invention is poor, [they] are hard to impregnate in the above resins and are easily impregnated in the carriers for fragrance impregnation used in this invention. However, affinity with fragrance-impregnable bodies according to magnitudes of polarity is relative. The extent of it is that the group of components in the blended fragrances having low polarity have relatively higher affinity with the resins of this invention and the group of components for which this [polarity] is high have less affinity with these [resins], and is not to say that hydrocarbons necessarily are held only in the resins of this invention and alcohols are necessarily held only in the fragrance-impregnable bodies of this invention.

In the sintered bodies for fragrance impregnation used in this invention which are made of ethylene-vinyl acetate copolymer and have resin portions and space portions, the group of components in the blended fragrance having relatively low polarity is held relatively well in the above resin portions and the group of components of relatively high polarity is held in the space portions.

This invention presents slow-release fragrance agents made by impregnating blended fragrances comprising multiple fragrance components into composite impregnable bodies comprising one, two or more kinds of thermoplastic resins for fragrance impregnation and carriers for fragrance impregnation, or into sintered bodies made of ethylene-vinyl acetate copolymers, and impregnating the fragrance components of relatively low polarity in the blended fragrance primarily in the thermoplastic resins for fragrance impregnation or in the resin portions of the above sintered bodies, and impregnating the fragrance components of relatively high polarity in the above blended fragrance primarily in the carriers for fragrance impregnation or placing [them] primarily in the spaces in the above sintered bodies.

That is, this invention presents slow-release fragrance agents, characterized by the fact that blended fragrances are impregnated in composite impregnable bodies wherein thermoplastic resins for fragrance impregnation have been mixed into carriers for fragrance impregnation and low polarity single fragrances of high volatility are impregnated selectively in the thermoplastic resins for fragrance impregnation.

With this invention, the labor of dividing the blended fragrances comprising multiple fragrance components beforehand into 2 or more component groups according to magnitudes of polarity and separately impregnating the high polarity component group in the resins of this invention and the low polarity component group in the carriers for fragrance impregnation of this invention is eliminated. That is, by impregnating the blended fragrances, without dividing [them] in any way, into the composite impregnable bodies of this invention (also without dividing these), impregnation is accomplished selectively due to the effects of the fragrance components

of good affinity and the impregnable bodies. Of course, fragrance components can be divided beforehand and impregnated in this invention.

Concrete methods for the "impregnation" performed in implementing this invention include all methods normally conducted in said industry such as dropping fragrance solutions on the impregnable body, immersing the impregnable body in the fragrance solution for a certain period, or spraying the fragrance solution on the impregnable body.

With this invention, powdered, finely granulated, granulated, thin-film, mesh or plate-shaped polyethylene, ethylene-vinyl acetate copolymer, ethylene-ethyl acrylate copolymer, polyvinyl chloride, polyvinyl acetate, polyethyl and methyl acrylate, polyethyl and methyl methacrylate, polyamide, polypropylene and polystyrene can be used for the thermoplastic resin for fragrance impregnation. The carriers for fragrance impregnation can be any material that can absorb liquid. Inorganic porous materials such as gypsum, silicate salts, active carbon, ceramic or alumina and filter paper, nonwoven fabric, felt and boards are preferable. 40% or less with respect to the carrier for fragrance impregnation is desirable for the mixing proportions for the thermoplastic resins for fragrance impregnation and 5-150% for the amount of fragrance added.

For the thermoplastic resins for fragrance impregnation and carriers for fragrance impregnation used in this invention, there are the following forms.

(a) Forms for the thermoplastic resins for fragrance impregnation

1. Powders
2. Fine granules or granules
3. Thin films or plates
4. The resins of 3 with random holes or mesh

(b) Forms for the carriers for fragrance impregnation

1. Powders of inorganic porous materials such as gypsum, ceramic, silicate salts, active carbon or alumina
2. Fine granules or granules of inorganic porous materials such as gypsum, ceramic, silicate salts, active carbon or alumina
3. Plates or agglomerations of inorganic porous materials such as gypsum, ceramic, silicate salts, active carbon or alumina
4. Thin films, plates or agglomerations of filter paper, nonwoven fabric, felt or boards

For the composite impregnable bodies of this invention, substrates made from combinations of one each or multiples of the forms given in (a) and (b) can be used. Compression moldings of powdered, fine granular or granular mixtures can also be used simultaneously.

Examples of blended fragrances used in this invention are given next.

Preparation Example 1 Blended rose fragrance

Limonene	20 parts
Linalol	70 "
Undecylenic aldehyde	30 "
Citronellol	250 "
Geraniol	200 "
Phenylethyl alcohol	200 "
Hydroxycitronellal	20 "
n-Hexyl alcohol	40 "
t-2-Hexenyl acetate	30 "
t-2-Hexenol	60 "
Ethyl caproate	30 "
Phenylethyl phenylacetate	30 "
Phenylethylacetate	<u>20 "</u>
	1000 "

Preparation Example 2 Blended kinmokusei [transliteration] fragrance

Methyldihydrojasmonate	20 parts
$\gamma$ -Decalactone	20 "
$\alpha$ -Ionone	50 "
Benzyl alcohol	50 "
Geraniol	80 "
Linalol	250 "
cis-3-Hexenyl isovalerate	10 "
Linalol oxide	80 "
Nonyl aldehyde	20 "
n-Hexyl alcohol	90 "
Amyl butyrate	160 "
Ethyl caproate	30 "
cis-3-Hexenol	100 "
Ethyl enantate	<u>40 "</u>
	1000 "

As above, by using composite fragrance-impregnable bodies, the invention maintains constant aromas over long periods for any blended fragrances by selectively and automatically

impregnating volatile nonpolar single fragrances in thermoplastic resins for fragrance impregnation. This is explained below using application examples.

#### Application Example 1

As an example of a composite fragrance-impregnable body, an impregnable body wherein 0.125 g of 40-mesh ethylene-vinyl acetate copolymer (10 % vinyl acetate content, called EVA below) powder had been glued evenly between 8-layer nonwoven fabric of 0.5 cm thickness and 7 cm x 7 cm size was used. 8 g ethyl caproate that was easily impregnated in EVA and was highly volatile were impregnated, and volatilization tests were conducted. As the results in Figure 1 show, clear differences from nonwoven fabric that did not use EVA were seen and marked slow-release effects were seen.

#### Application Examples 1 and 2 [sic]

When the blended fragrances of Preparation Example 1 or 2 were impregnated in the composite fragrance-impregnable bodies used in Reference Example 1, the initial aroma was maintained even one month after impregnation. But with nonwoven fabric that was not treated with EVA, a clear change in aroma was seen 1 week after impregnation. Those results are shown in Figures 2 and 3.

#### Application Example 3

25 g per m<sup>2</sup> of 40-mesh EVA powder were glued evenly onto nonwoven fabric (80 g/m<sup>2</sup> standard weight). 10 layers of this were laid on top of each other to make a thickness of 0.6 cm. This was cut to 7 cm x 7 cm. In the EVA nonwoven fabric composite impregnable body thus obtained, 10 g of blended kinmokusei fragrance were impregnated by adding dropwise, and a slow-release fragrance agent was obtained.

#### Application Example 4

100.0 parts by weight of hemihydrate gypsum (JIS Grade A calcined gypsum) and 0.5 parts by weight of 40-mesh EVA powder were added to 80.0 parts by weight water and mixed and stirred. After this was poured into a container of 1 cm x 5 cm x 5 cm and cured, this cured product was removed from the container and dried for 48 h at 40°C. 8 g of blended rose fragrance was impregnated by adding dropwise in the plate-shaped EVA-gypsum composite impregnable body thus obtained and a slow-release fragrance agent was obtained.

As a result of the application examples, it was found that volatile nonpolar fragrances impregnated in thermoplastic resins for fragrance impregnation were hard to volatilize.



### Brief description of the figures

Figure 1 shows the results of volatilization tests when ethyl caproate was used as a single fragrance and was impregnated in EVA-treated nonwoven fabric and non-EVA-treated nonwoven fabric, respectively.

Figure 2 shows the results of volatilization tests when the blended fragrance of Preparation Example 1 was impregnated in EVA-treated nonwoven fabric and untreated nonwoven fabric.

Figure 3 shows the results of volatilization tests when the blended fragrance of Preparation Example 2 was impregnated in EVA-treated nonwoven fabric and untreated nonwoven fabric.

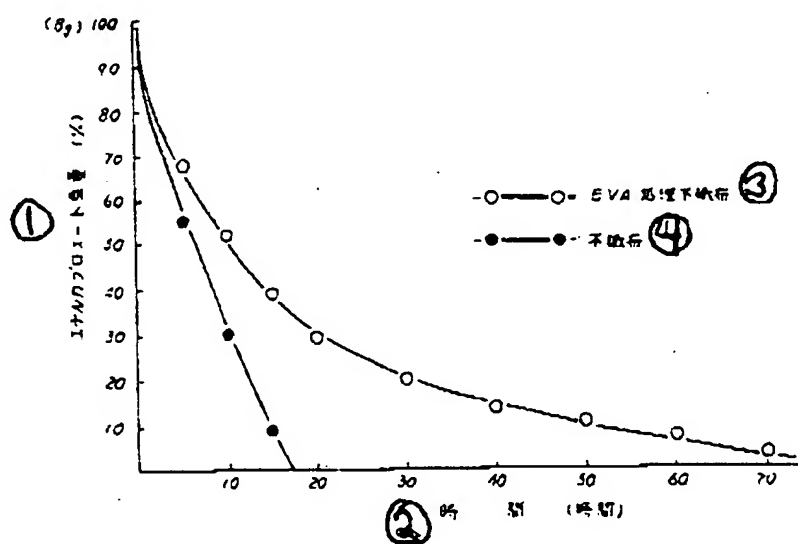


Figure 1

- Key:
- 1 Weight of ethyl caproate (%)
  - 2 Time (h)
  - 3 EVA-treated nonwoven fabric
  - 4 Nonwoven fabric

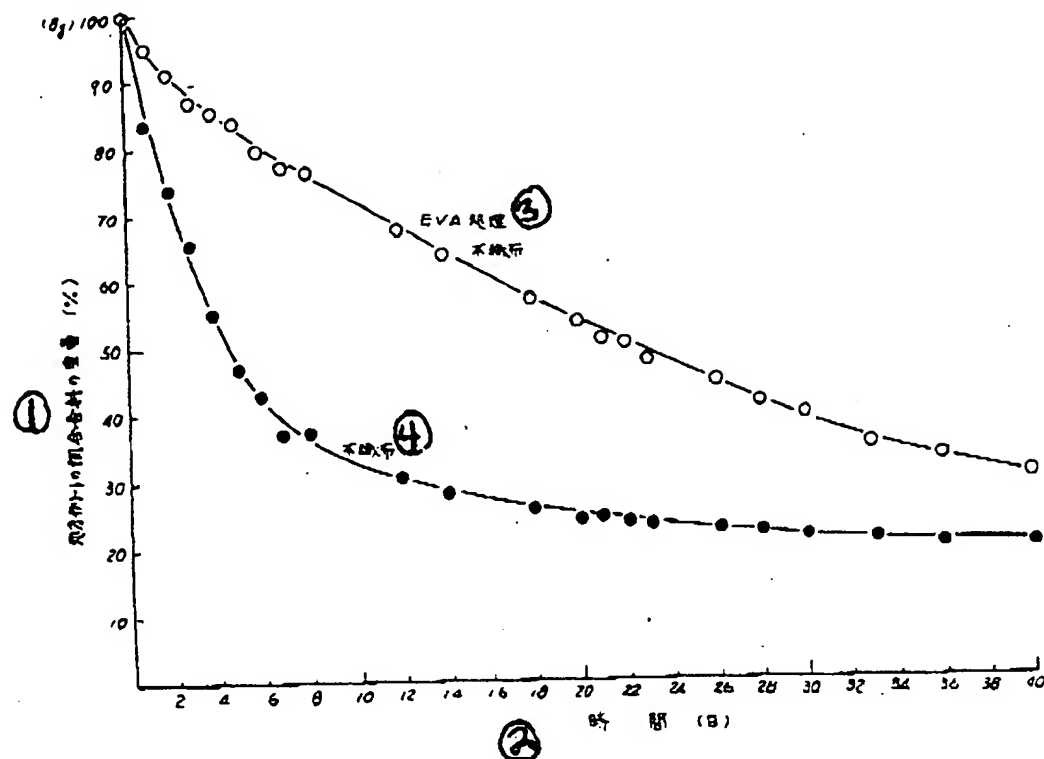


Figure 2

- Key:
- 1 Weight of Preparation Example 1 blended fragrance (%)
  - 2 Time (days)
  - 3 EVA-treated nonwoven fabric
  - 4 Nonwoven fabric

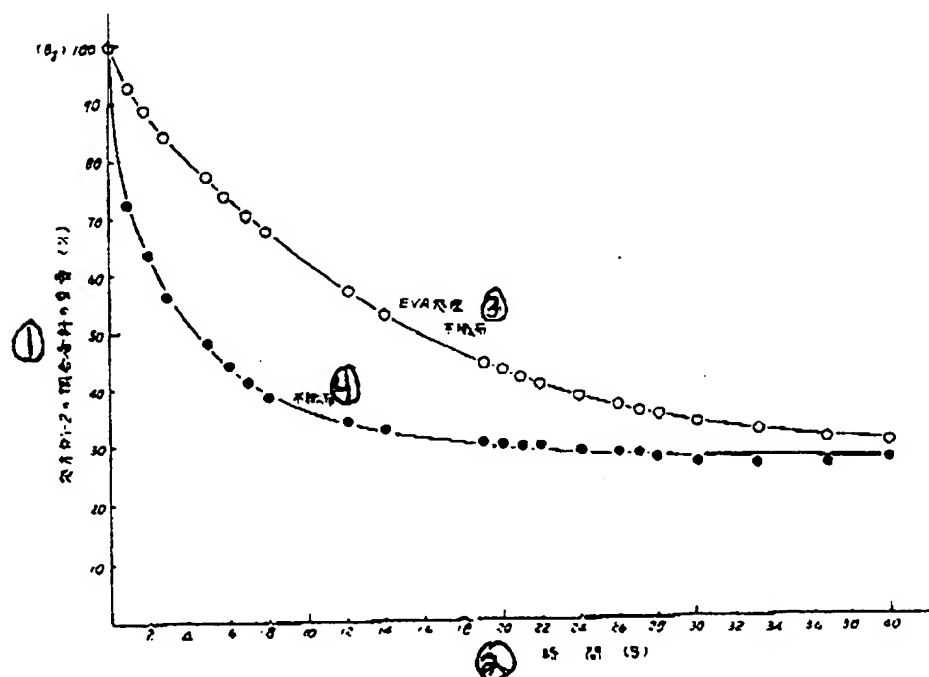


Figure 3

Key: 1 Weight of Preparation Example 2 blended fragrance (%)  
2 Time (days)  
3 EVA-treated nonwoven fabric  
4 Nonwoven fabric

## SPECIFICATION

### 1. Title of the Invention

Air-permeable deodorizing or scented film

JP 62153324

### 2 Claims

- (1) An air-permeable deodorizing or scented film, comprising a polyolefin resin composition that contains polyolefin resin, a filler, a modifier, and a deodorizing agent or scent, subjected to melt forming and then to a stretching process.
- (2) The air-permeable deodorizing or scented film according to claim 1, wherein the composition contains, per 100 parts by weight of polyolefin resin, the filler in proportions of from 25 to 400 parts by weight, the modifier in proportions of from 1 to 50 parts by weight, and the deodorizing agent or scent in proportions of from 0.01 to 10 parts by weight.
- (3) The air-permeable deodorizing or scented film according to claim 1, wherein the stretching process is uniaxial stretching or biaxial stretching, the stretch ratio being at least 1.1 in one axial direction.
- (4) The air-permeable deodorizing or scented film according to claim 1, wherein air permeability as measured in accordance with JIS P8117 is from 20 sec/100 cc to 3000 sec/100 cc, and moisture permeability as measured in accordance with JIS Z0208 (40°C, 90% RH) is 800 g/m<sup>2</sup> · 24 hr or above.
- (5) The air-permeable deodorizing or scented film according to claim 1, wherein water pressure resistance is 1 mH<sub>2</sub>O or higher.

### 3 Detailed Description of the Invention

#### Field of Industrial Utilization

The present invention relates to a film having deodorizing properties or scent, and endowed with air permeability.

#### Prior Art

The mechanism of deodorizing action of deodorizing materials may be broadly categorized into three types: physical deodorizing, chemical deodorizing, and biological deodorizing. Such materials have been used independently, and attempts have also been made to compound them with thermoplastic resins to produce films or sheets. Compounding of scents with thermoplastic resins has also been tried.